

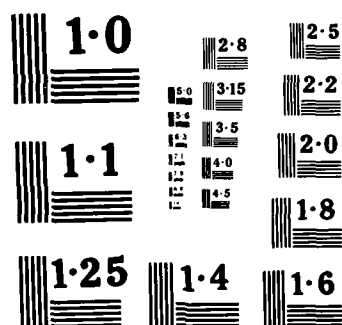
NITROGEN ANALYSIS BY CHEMILUMINESCENCE(U) AIR FORCE
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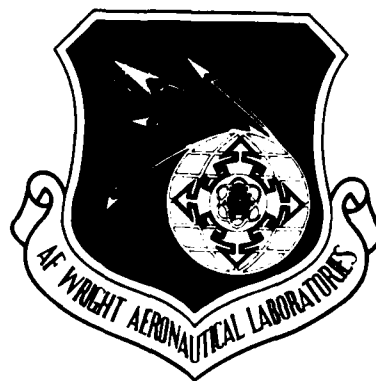
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NITROGEN ANALYSIS BY CHEMILUMINESCENCE

Richard C. Striebich, 1Lt, USAF

Fuels Branch
Fuels and Lubrication Division

April 1985

Final Report for Period August 1982 - December 1983

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20. Abstract (Continued)

by two different chemiluminescent detection systems, as well as by the microkjeldahl and microcombustion methods. Results clearly point out the ability of the chemiluminescent method to measure the nitrogen level of low ppm shale-derived aviation turbine fuel.

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FOREWORD

This technical report describes an experimental study of the possible limitations of a new instrumental technique for the determination of organically bound nitrogen in liquid samples by chemiluminescence. The work reported here was performed in-house under Work Unit 30480591, "Fuel Evaluation and Development" which is administered by the Fuels Branch (POSF), Fuels and Lubrication Division (POS), Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

The work described herein was performed by Lt Richard Striebich from September 1982 to December 1983. Special acknowledgement is extended to members of the Fuels Branch (POSF) as well as the Fuels Technical Support Branch (POFF) for their guidance and encouragement.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CRI	Constant Rate Injector
C	Degrees Celsius
DMA	Dimethylaniline
DMQ	2,7-Dimethylquinoline
1EP	1-Ethylpiperidine
F	Degrees Fahrenheit
MV-sec	Millivolts per second
N	Nitrogen
NO	Nitric Oxide
ng	nanogram (10^{-9} grams)
nm	nanometers (10^{-9} meters)
PM	Photomultiplier
ppm	parts-per-million
PYD	Pyridine
μ l	microliters

SECTION I

INTRODUCTION

Nitrogen compounds are detrimental to the thermal and storage stability of aviation turbine fuel. Nitrogen-bearing deposits are formed readily when a fuel which contains heteroatoms such as nitrogen is thermally stressed (Reference 1). In work completed for the Aero Propulsion Laboratory in 1967, Taylor describes increasing rates of deposit formation with increasing nitrogen concentration (Reference 2) (Figure 1). Since deposits tend to plug combustor nozzles and reduce heat flow in an aircraft engine fuel system, it would be advantageous to monitor the amount of organically bound nitrogen in a jet fuel.

Since total nitrogen content is greater in future non-petroleum fuel sources such as oil shale, tar sands, and coal liquids, monitoring the nitrogen level in distillate fuels will become more crucial. In addition to concerns of thermal and storage stability, nitrogen compounds poison catalysts, making hydrogenation processing more inefficient and expensive. Naturally, these alternative sources of fuel, when combusted, produce an increase in NO_x emissions unless nitrogen levels are monitored and controlled during hydrotreating.

The purpose of this report is to validate the accuracy and precision of the ANTEK Model 720 Chemiluminescent Nitrogen Detector. This instrument is designed to detect organically bound nitrogen in concentrations ranging from one part-per-million (weight/weight) to approximately 10,000 ppm nitrogen (1.0 wt. % nitrogen).

Until just recently, elemental nitrogen has been measured almost exclusively by the Kjeldahl method. In the Kjeldahl method, boiling sulfuric acid is used to convert nitrogen to ammonia which is subsequently titrated. This method is hazardous and somewhat lengthy, and can give inaccurate results for low ppm nitrogen samples. In the past few years, a number of systems have been developed to measure nitrogen at the ppm level. Microcoulmetry (ASTM 3431) and gas chromatography with nitrogen selective detector are two widely used methods. Chemiluminescence, however, is becoming more and more popular because of its wide range of applicability (0 to 10,000 ppm N), analysis time (less than five minutes per sample), and excellent accuracy and precision.

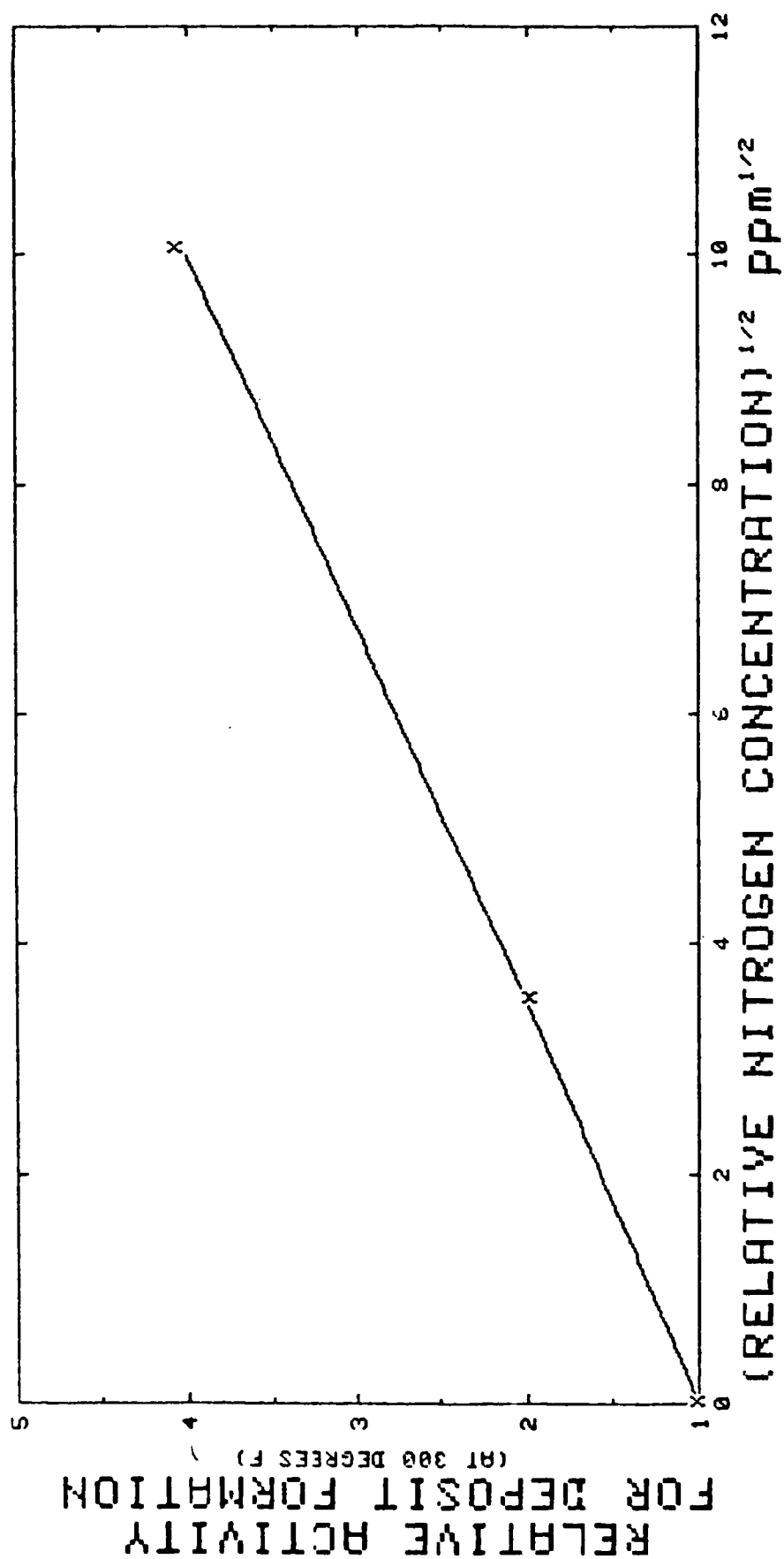


Figure 1. Activity for Deposit Formation vs. Nitrogen Concentrations in Fuel

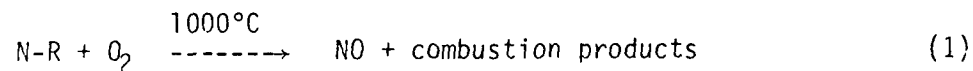
SECTION II

CURRENT RESEARCH

1. EXPERIMENTAL

a. Theory

In the chemiluminescent process, nitrogen-bearing compounds are pyrolyzed at high temperatures to form nitric oxide:



At these temperature conditions, the formation of NO is greatly favored regardless of the physical or chemical state of the nitrogen. Temperatures of 1000 degrees C or higher tend to give the highest conversion of organically-bound nitrogen to nitric oxide (Figure 2).

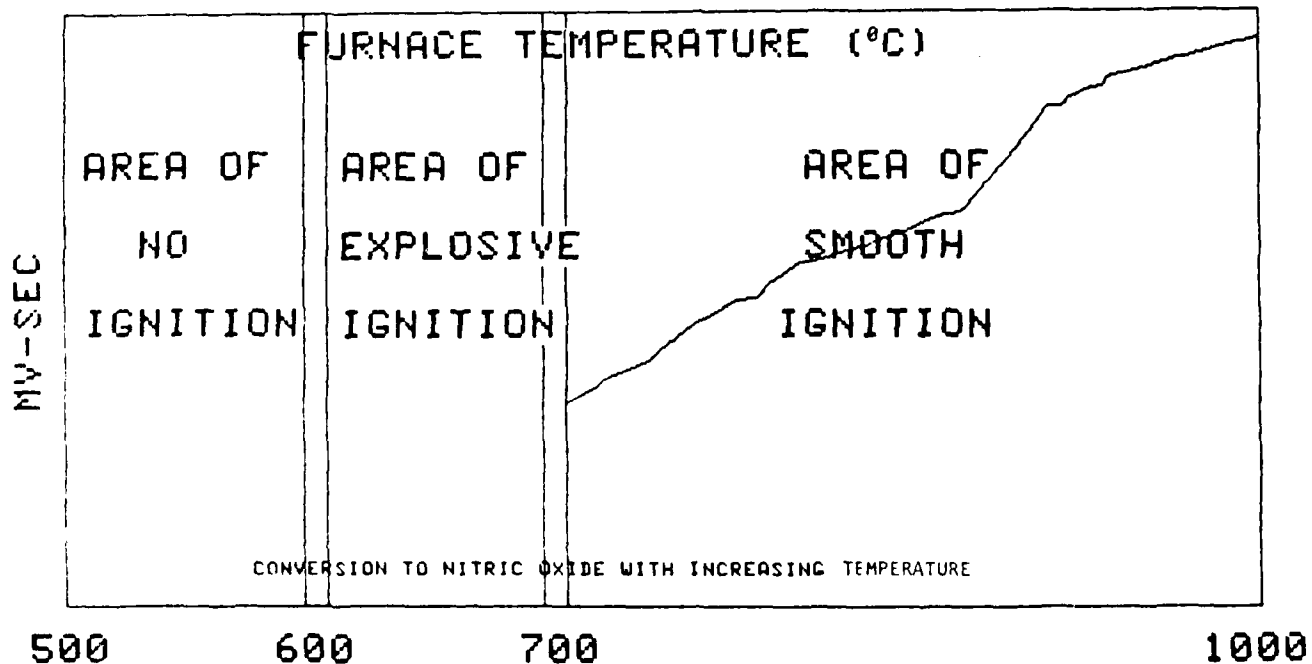


Figure 2. Conversion of Nitrogen to Nitric Oxide

DATA AND CALCULATIONS

The raw data (area counts vs. nanograms nitrogen injected) were incorporated into the RESULTS section.

Parts-per-million (ppm) nitrogen was determined on a weight-to-weight basis:

$$\text{ppm nitrogen} = \frac{\text{weight solute (nitrogen)}}{\text{weight of solvent}} \times 10^6 = \frac{\text{ng N}}{\text{mg solvent}} \quad (4)$$

The detector for the nitrogen analyzer generates integration counts which are graphed against nanograms nitrogen injected to construct a calibration curve. Nanograms nitrogen injected were calculated by:

$$\frac{\text{ng N}}{\text{ng solvent}} \times \rho \text{ solvent} \times \text{sample size } (\mu\text{l}) = \text{ng Nitrogen} \quad (5)$$

$$\text{where } \rho = \text{density: } \frac{\text{mg solvent}}{\mu\text{l solvent}}$$

RESULTS

a. Model Mixture Studies

Table 3 lists each solute and solvent in the model mixture study. The average number of nanograms nitrogen injected is plotted against the average area count for each mixture. A least squares fit provides the best straight line through the data; the slopes, intercepts, and correlation coefficients are reported. Figures 10 and 11 graphically depict these data. These figures were used as calibration curves for the second part of the experiment.

b. Standard Addition Studies

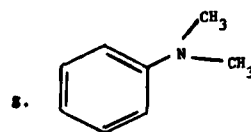
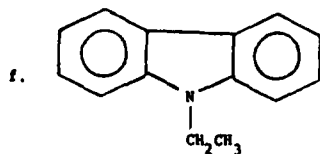
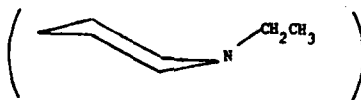
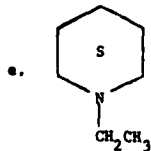
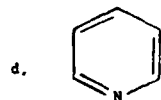
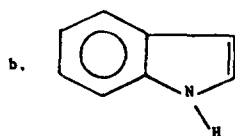
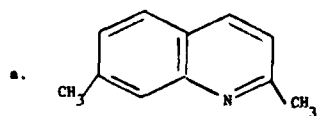
Table 4 lists the known vs. measured values for the shale fuel additions. Figure 12 describes these data graphically.

TABLE 2
STANDARD ADDITIONS TO SHALE JP-4

CODE	Nitrogen from 2,7-dimethylquinoline (ppm N)	Nitrogen from Pyrrole (ppm N)	Nitrogen from 1-ethylpiperidine (ppm N)	Nitrogen from Dimethylaniline (ppm N)	Nitrogen from Pyridine (ppm N)	Total Nitrogen added (sum of last five columns) (ppm N)
JP4-1	0	0	0	0	0	0
JP4-2	1.81	2.64	1.33	1.44	1.13	8.35
JP4-3	3.62	5.28	2.66	2.88	2.26	16.70
JP4-4	18.05	13.19	13.32	14.44	11.26	70.26
JP4-5	36.10	26.38	26.64	28.88	22.52	140.52
JP4-6	6.37	4.66	5.89	6.38	4.98	28.28

TABLE 1
SOLUTES, SOLVENTS AND CONCENTRATIONS
MODEL MIXTURE STUDIES

SOLUTES	SOLVENT	ppm levels (wt/wt)
2,7-Dimethylquinoline (a)	Toluene	3.2, 31.8, 159.3, 637.2, 1593
Indole (b)	Toluene	3.1, 31.2, 156.1, 624.4, 1561
Pyrrole (c)	Toluene	4.7, 46.6, 232.8, 698.4, 1164
Pyridine (d)	Isooctane	2.5, 24.9, 124.5, 497.8, 1244.5
1-ethylpiperidine(e)	Isooctane	3.0, 29.5, 147.3, 589.2, 1473
N-ethylcarbazole (f)	Toluene	2.9, 29.4, 147.1, 588.4, 1471
Pyrrole (c)	Toluene	4.7, 46.6, 232.8, 698.4, 1164
N,N-dimethylaniline (g)	Isooctane	3.2, 31.9, 159.6, 638.4, 1596



because the sample was already quite dilute. The larger injection volume provided more nanograms of nitrogen which increased the detectability of the sample. In either low or high ppm samples, five to ten measurements were taken for each sample with an average deviation of plus or minus 3% (relative).

e. Experimental Design

This experiment consisted of two tasks: first, to show the linearity of detector response with respect to nitrogen concentration as well as to demonstrate a non-dependence of detector response on compound type; secondly, to determine detector response for organically-bound nitrogen in a complex shale JP-4 fuel matrix.

(1) Model Mixture Studies: Though many nitrogen compounds were available, only those classes of compounds found in jet fuels were used, i.e., pyrroles, amines, indoles, pyridines, and quinolines (Reference 5). A stock solution of each solute was prepared and diluted so that five different solutions were available with ppm nitrogen values ranging from 2 to 1500 ppm N (wt/wt). Solutes, solvents, and concentrations are given in Table 1. These solutions were then analyzed at the conditions specified earlier. A least squares curve fit of the data for the 40 different model mixtures was then constructed and used as a calibration curve for further experiments.

(2) Standard Addition Studies: Instead of using isooctane or toluene solvents, shale-derived JP-4 provided a more complex matrix in the second part of the experiment. Aliquots of five of the nitrogen-bearing standards used in the model mixture study were blended into the shale fuel to produce four mixtures that were 9 to 150 ppm added nitrogen. A standard solution containing several nitrogen compounds in isooctane was also prepared as well as a control sample of JP-4 (without additives) (Table 2).

By obtaining a calibration curve from the model mixture experiments, the nitrogen content of the shale fuel sample could then be measured.

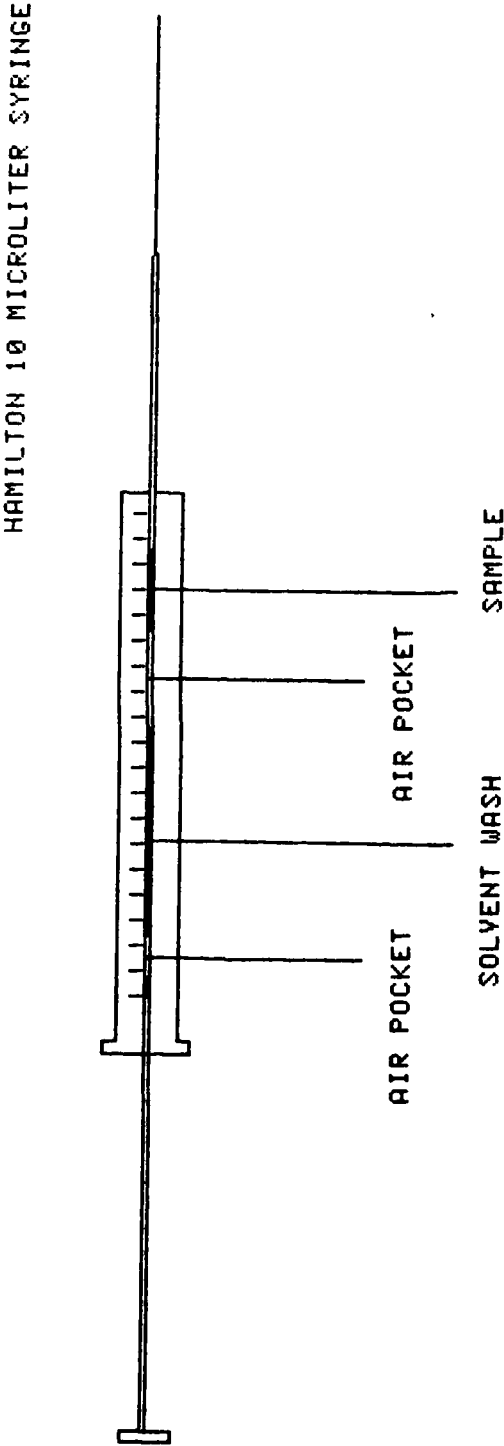


Figure 9. Syringe Loading Technique

(2) Furnace Temperature: A non-feedback, manual setting controlled the power supply to the furnace heating elements. A setting of 7.5 created a furnace temperature of 1000 degrees C.

(3) Range and Sensitivity: A low and high range were available. Since the experiment concentrated on a range of 0 to 1500 ppm nitrogen, the low range was appropriate for all measurements. The high setting could be utilized for high nitrogen crudes and only slightly refined products. Sensitivity levels of 1, 10, 20, and 50 were available: concentrations of 0-80 ppm nitrogen usually required a sensitivity of 1. Approximately 80 to 800 ppm required a sensitivity of 10 and above 800 generally needed a level of 20.

(4) Injection Rate: Injection rate was probably the most crucial parameter to control. Too high an injection rate caused coking of the sample within the combustion tube. A rate of 11 μ l/min was normally used because this rate maximized response and was suggested by other experimenters (Reference 4).

d. Operating Procedure

Gas flow rates and rotometer settings were first established as described in Section 2. c, "Operating Conditions." Injections were made with detector control in the "on" position. Syringe injection technique had a significant impact on the accuracy and precision of a nitrogen determination.

(1) Syringe Technique: To ensure that the entire sample was transferred from the syringe to the combustion furnace, a 2 - 3 μ l pocket of solvent (toluene) was placed behind a 1 - 2 μ l pocket of sample in the syringe, as shown in Figure 9. The solvent served to "rinse" the sample out of the syringe. Since this technique was employed for all samples, (with the exception of extremely low ppm nitrogen samples) the possible effect of solvent dilution was not observed in the calibration curve. Further, since the detector response was plotted versus the number of nanograms of nitrogen detected, no dilution effect was present.

(2) Syringe Technique (low ppm N samples): If the solution to be analyzed was suspected to be low in nitrogen content (less than 20 ppm), approximately 5.7 μ l was drawn into the syringe and injected. No solvent rinse was employed

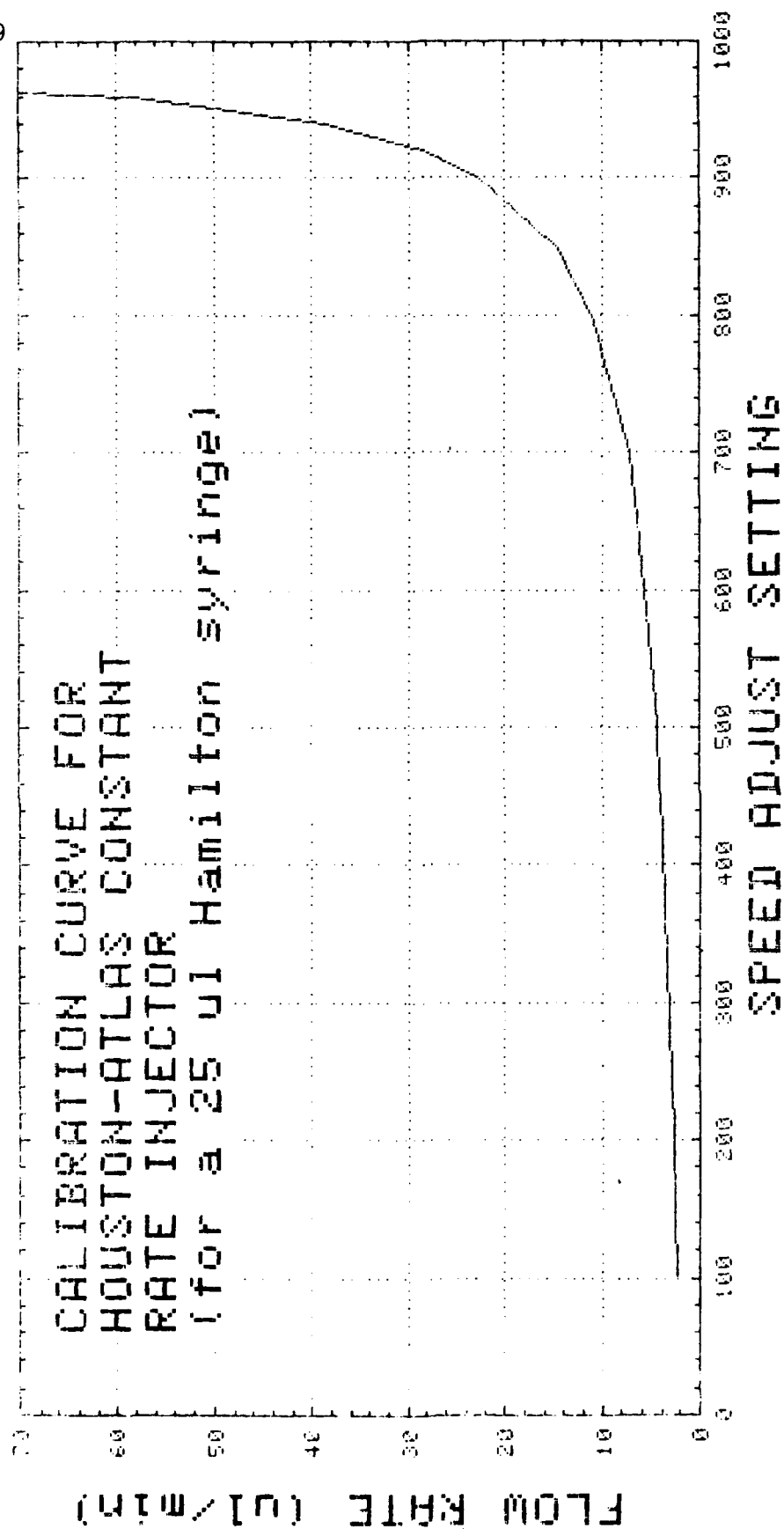


Figure 8. Calibration Curve for Constant Rate Injector

(4) Injection System: A Houston-Atlas Model 1001 constant rate injector (CRI) forced the sample out of a 10 μ l Hamilton syringe. A digital rate setting on the CRI controlled the speed of sample introduction. The calibration curve relating digital setting to volumetric flow rate for a 10 μ l syringe is included in Figure 8.

(5) Detection System: One-sixteenth inch O.D. teflon tubing and quartz connectors allowed transfer of hot pyrolysis gases from the combustion tube to the reaction chamber. The ozone generator separated and recombined oxygen molecules to form ozone at high temperatures. Ozone and combustion gases combined in a reaction chamber to give off light which was detected by a photomultiplier (PM) tube. The resulting signal was electrically transferred to an integrator and strip chart recorder. The detection system also included zero baseline adjustment, diagnostic lights, as well as different sensitivity settings (Figure 4).

(6) Gas Scrubbers: Gases from the reaction chamber were transferred to a scrubber of activated charcoal and indicating drierite. The charcoal adsorbed any nitrogen dioxide or ozone present in the gas stream after leaving the detection system. When the charcoal was completely saturated with adsorbed gases, the ozone would move into the section of the scrubber with indicating drierite. Since ozone turns indicating drierite black, the scrubber would then be ready to be recharged with fresh adsorbents.

c. Operating Conditions

Many of the operating conditions were obtained by varying conditions until maximum response (integration counts) was obtained for each injection. Other conditions were suggested by the manufacturers or their technical representatives.

(1) Gas flow rates: At the suggestion of ANTEK Instruments Inc., the oxygen flow rate was increased well beyond that which was initially suggested in the operating manual. The greater rate gave an increased response for an 80 parts-per-million nitrogen standard. Normally, the O_2 flow rate was 790 cc/min, (60 psi pressure), the argon flow rate was 47 cc/min (20 psi pressure), and the ozone flow rate was 120 cc/min. The pyrolysis system included a means of increasing the flow of oxygen to the inlet of the combustion tube; this means was not utilized in this experiment.

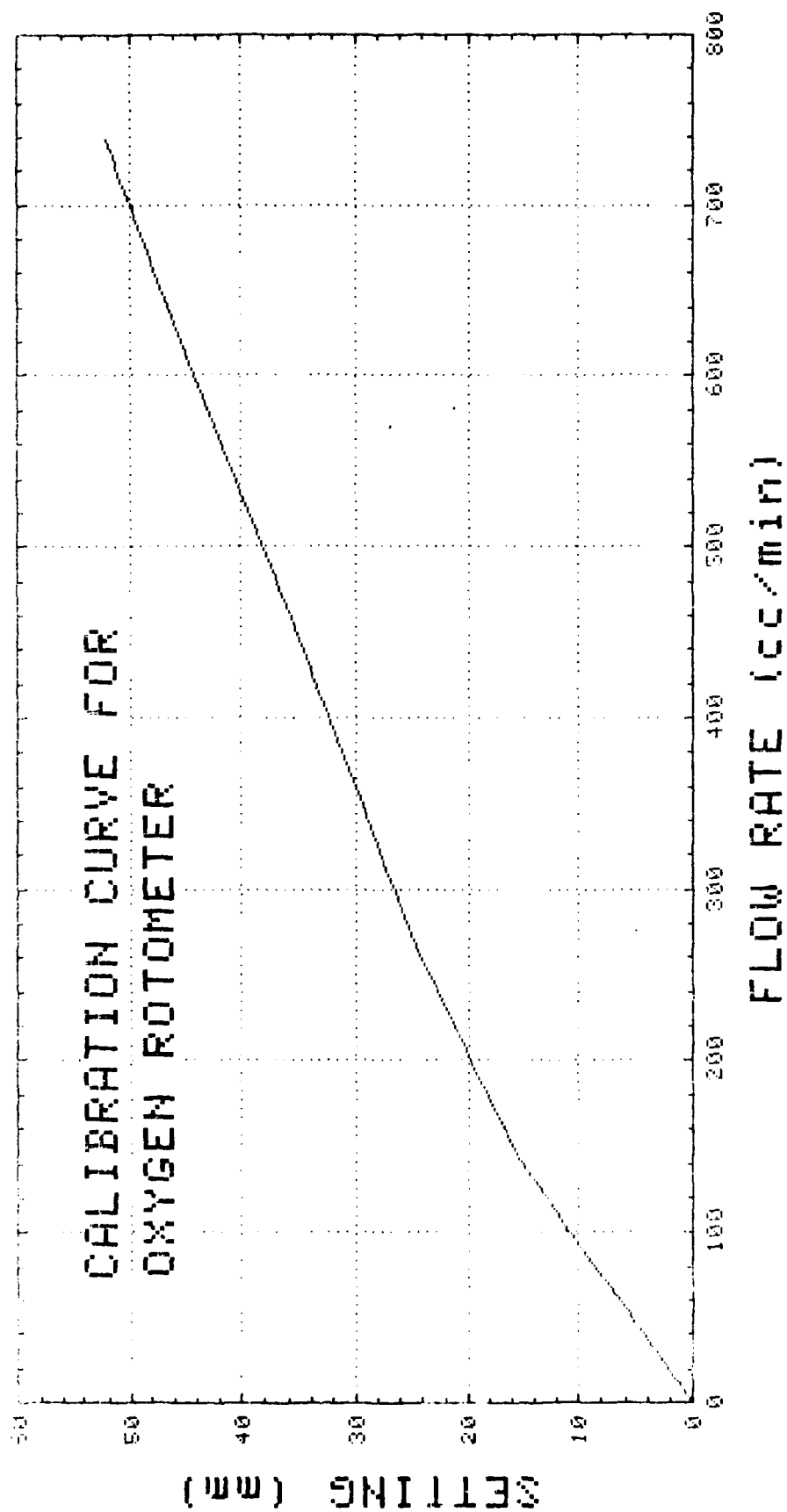


Figure 7. Calibration Curve for Oxygen Rotometer

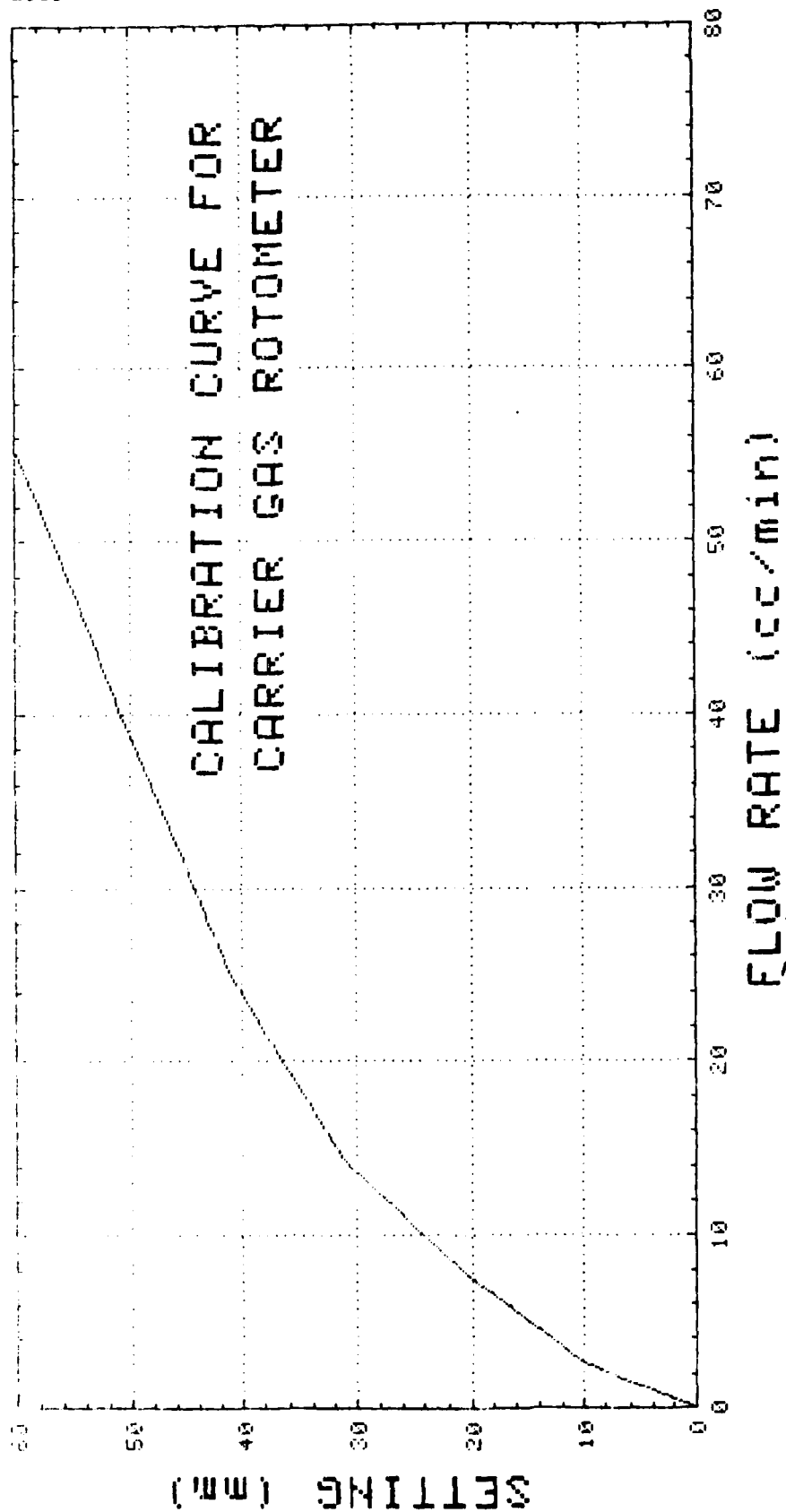


Figure 6. Calibration Curve for Carrier Gas Rotometer

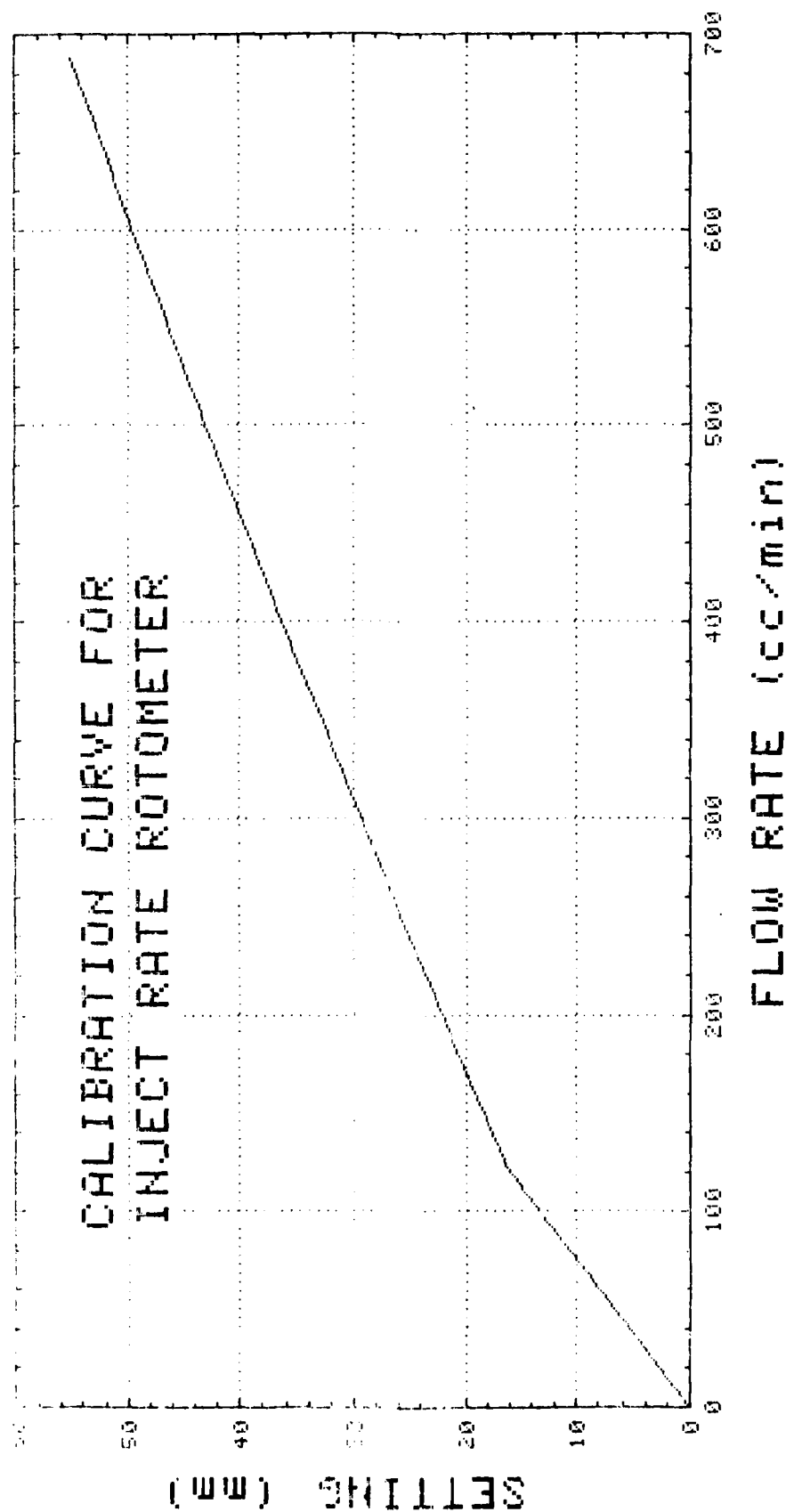


Figure 5. Calibration Curve for Inject Rate Rotometer

CHEMILUMINESCENT DETECTOR

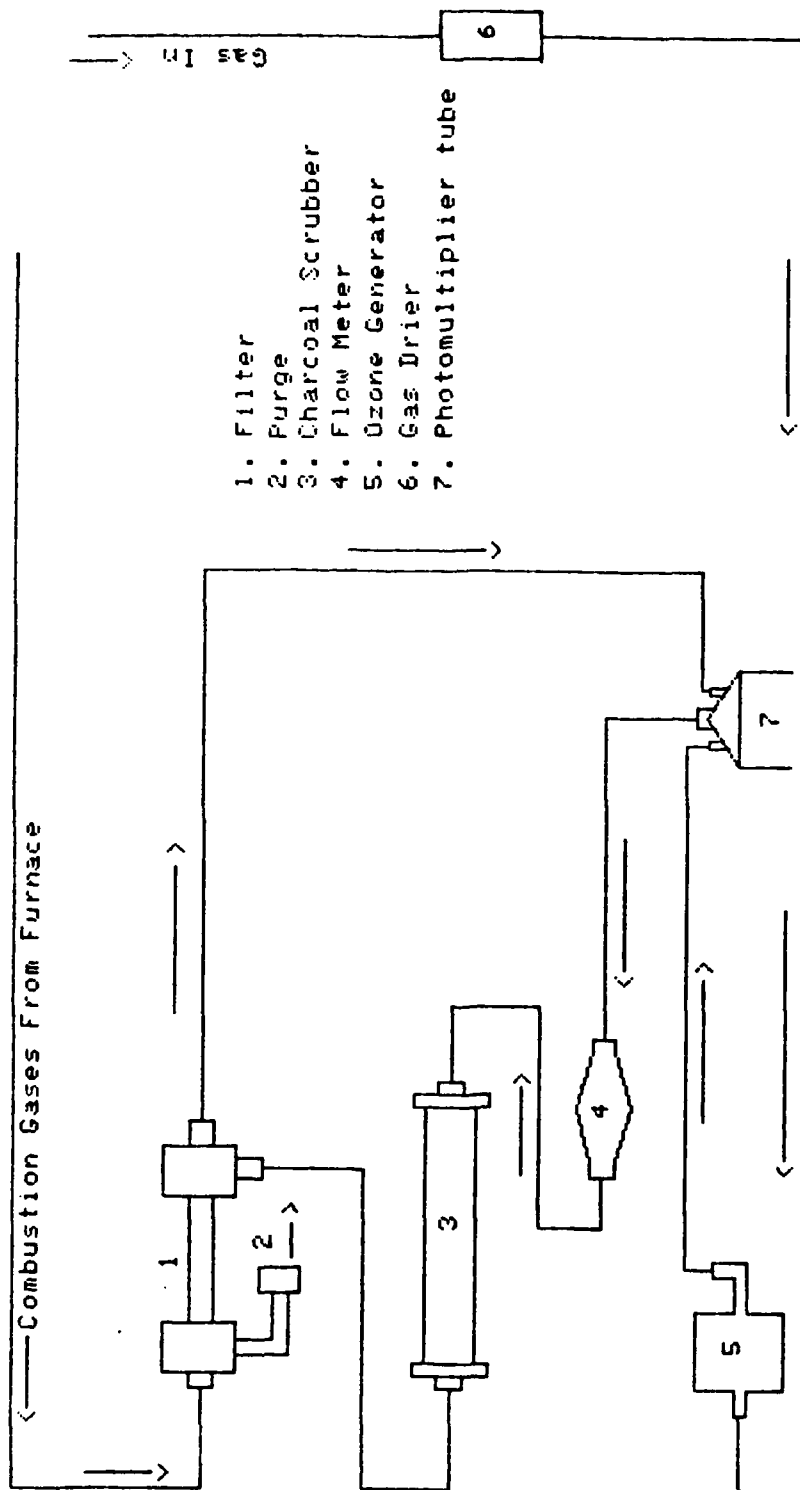


Figure 4. Chemiluminescent Detector

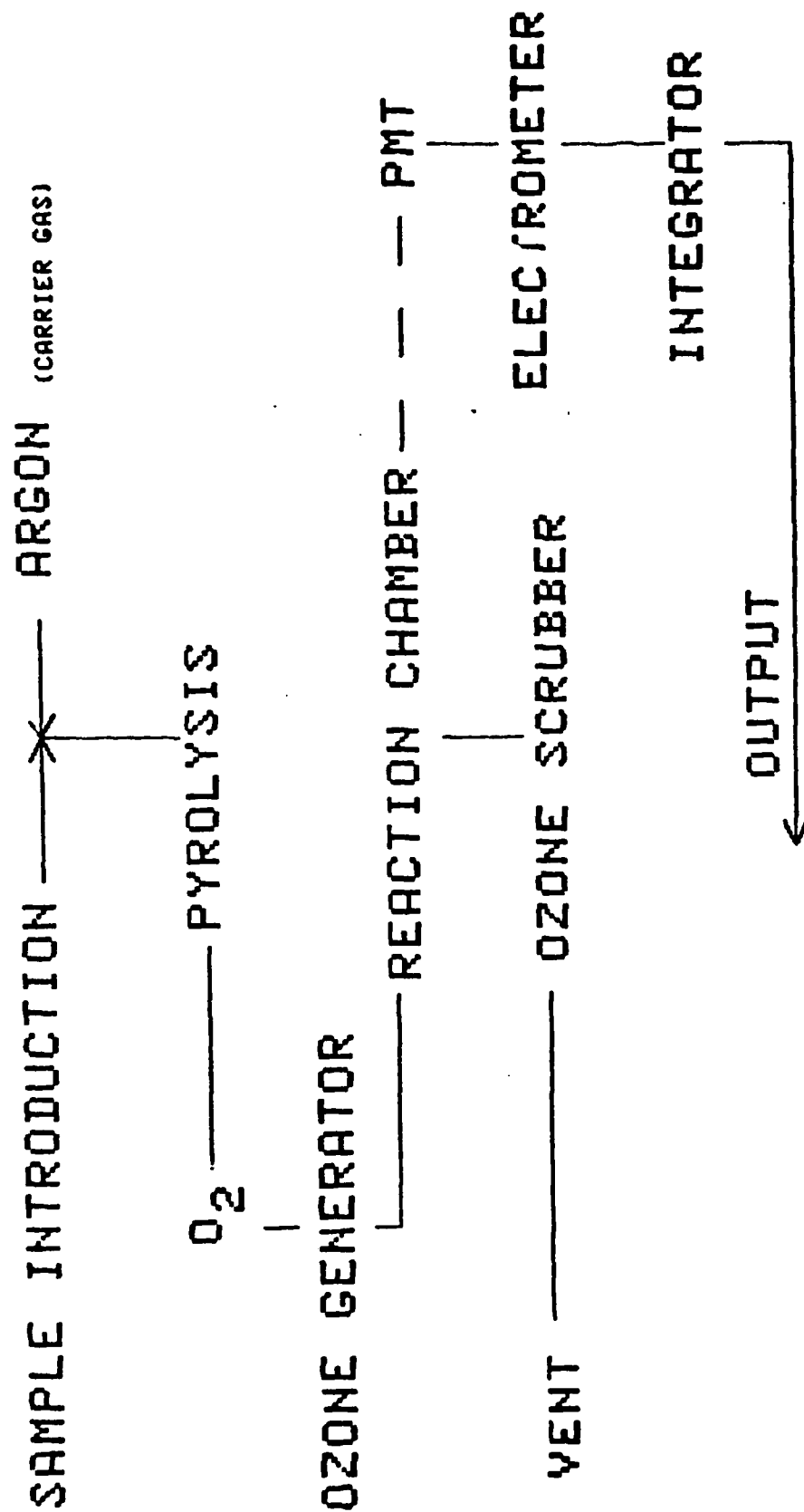
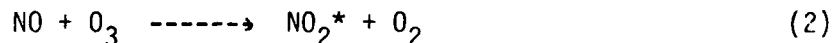


Figure 3. Chemiluminescent Detection System

Nitric oxide then combines with ozone accordingly:



Nitrogen dioxide (NO_2^*) is in an excited state. As its electrons fall to ground state energy, the molecule emits a photon in the 700 - 900 nm range:



The amount of light emitted with this wavelength can be quantitated with a light sensitive detector (photomultiplier tube) and is directly proportional to the amount of nitrogen in the sample.

b. Instrumentation

Diagrams of the chemiluminescent detection system and detector are shown in Figures 3 and 4. The major components of the system are described as follows:

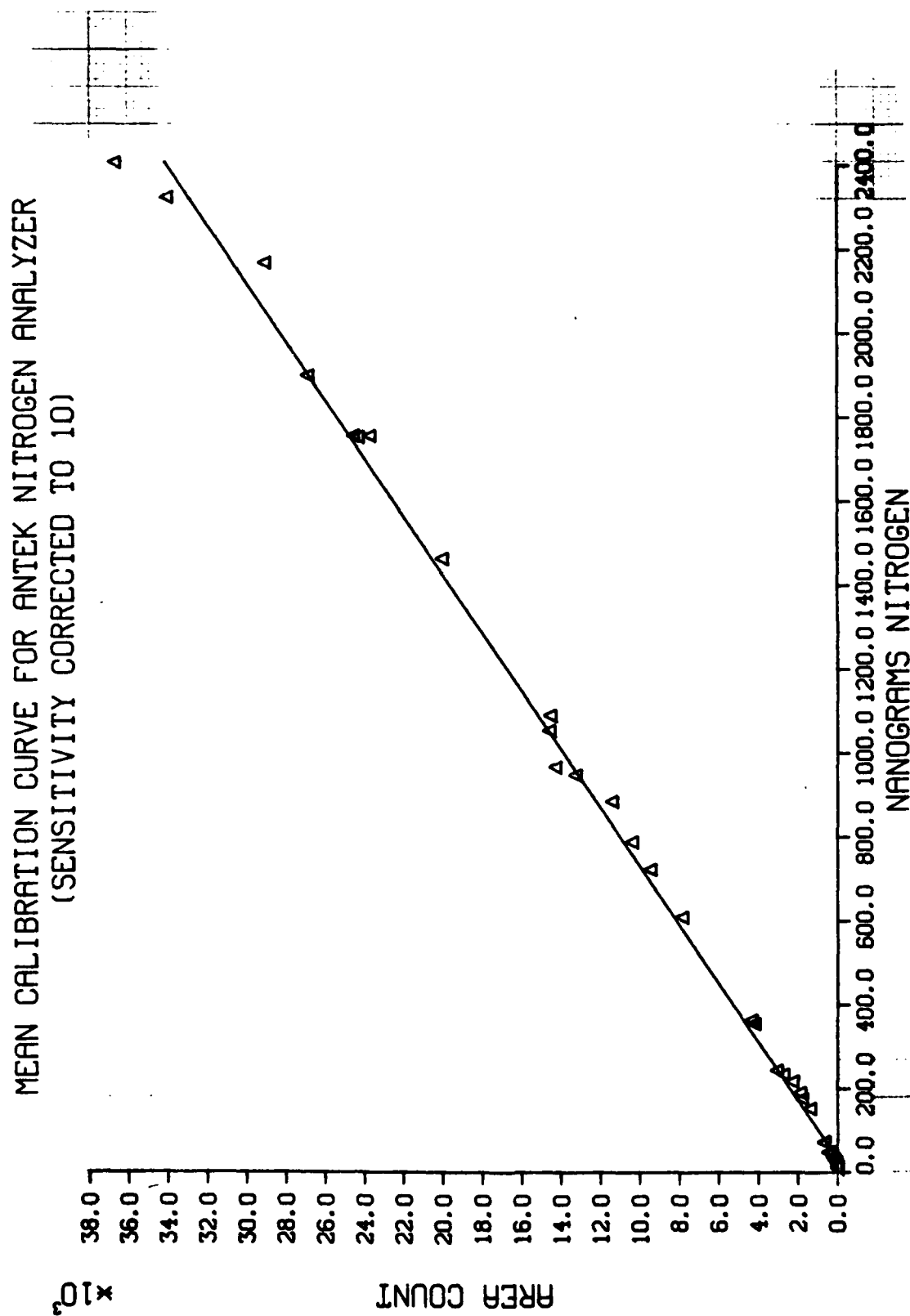
(1) Gases: Argon and oxygen (99.999% purity) were the only two gases required for this experiment. Gas filters of molecular sieve and indicating drierite removed water in both gas lines before introduction into the detector system. One branch of the oxygen line was connected to the ozone generator while another branch fed directly into the combustion tube. Rotometers just upstream of the combustion tube controlled gas flow rates (Figures 5, 6, and 7).

(2) Furnace: Although an ANTEK Model 771 pyroreactor was purchased along with the chemiluminescent detection system, this furnace could not be used. The heating elements burned out repeatedly due to the thermal shock of cycling the elements between low and high temperatures. A Lindberg Model 55035 tube furnace with a manual temperature controller (non-feedback) was a suitable substitution. This furnace, which had a single heating zone, required insulation to maintain constant temperature throughout the length of the pyrolysis tube.

(3) Pyrolysis Tube: The quartz pyrolysis tube could withstand temperatures exceeding 1100 degrees C without fracturing. Though some pyrolysis tubes are adaptable to a "boat" inlet technique (for high-boiling liquids and solids) this tube could only be used for syringe injection.

TABLE 3
RESULTS OF MODEL MIXTURE EXPERIMENTS

COMPOUND	SOLVENT	ng INJECTED	AREA COUNT (SENS = 10)	LEAST SQUARES FIT	CORRELATION COEFFICIENT
2,7 dimethylquinoline	Toluene	10.46	46.1	Slope: 15.329 Intercept = -349.4	0.9999
		48.7	504.6		
		243.1	3109.8		
		966.8	14304.7		
		2407.1	36639.1		
Indole	Toluene	10.77	27.0	Slope: 14.75 Intercept = -416.6	0.9998
		48.7	437.0		
		233.9	2765.3		
		947.5	13274.7		
		2323.4	34013.0		
Pyrrole	Toluene	15.28	58.0	Slope: 13.672 Intercept = -337.9	0.9999
		71.4	684.5		
		355.2	4232.6		
		1089.9	14558.3		
		1756.0	23727.2		
Pyridine	Isooctane	8.91	1.8	Slope: 13.880 Intercept = -380.7	0.9996
		29.9	178.4		
		152.6	1415.9		
		608.6	788.3		
		1464.0	20053.0		
1-ethylpiperidine	Isooctane	13.45	7.9	Slope: 14.043 Intercept = -406.5	0.9998
		35.9	240.8		
		176.2	1811.4		
		722.2	9508.6		
		1753.2	24328.0		
N-ethyl carbazole	Toluene	12.22	26.3	Slope: 13.524 Intercept = -365.18	0.9999
		45.9	353.8		
		216.8	2307.0		
		884.2	11445.7		
		2168.0	29038.0		
Pyrrole (rerun)	Toluene	23.43	86.7	Slope: 14.208 Intercept = -414.0	0.9998
		72.7	717.2		
		363.3	4387.0		
		1053.5	14619.6		
		1756.0	24564.4		
N,N dimethylaniline	Isooctane	12.71	20.6	Slope: 14.323 Intercept = -492.12	0.9996
		39.3	256.6		
		190.0	1902.6		
		787.8	10421.2		
		1899.6	26895.6		



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Figure 10. Mean Calibration Curve for ANTEK Nitrogen Analyzer

MEAN CALIBRATION CURVE FOR ANTEK NITROGEN ANALYZER
(SENSITIVITY CORRECTED TO 10)

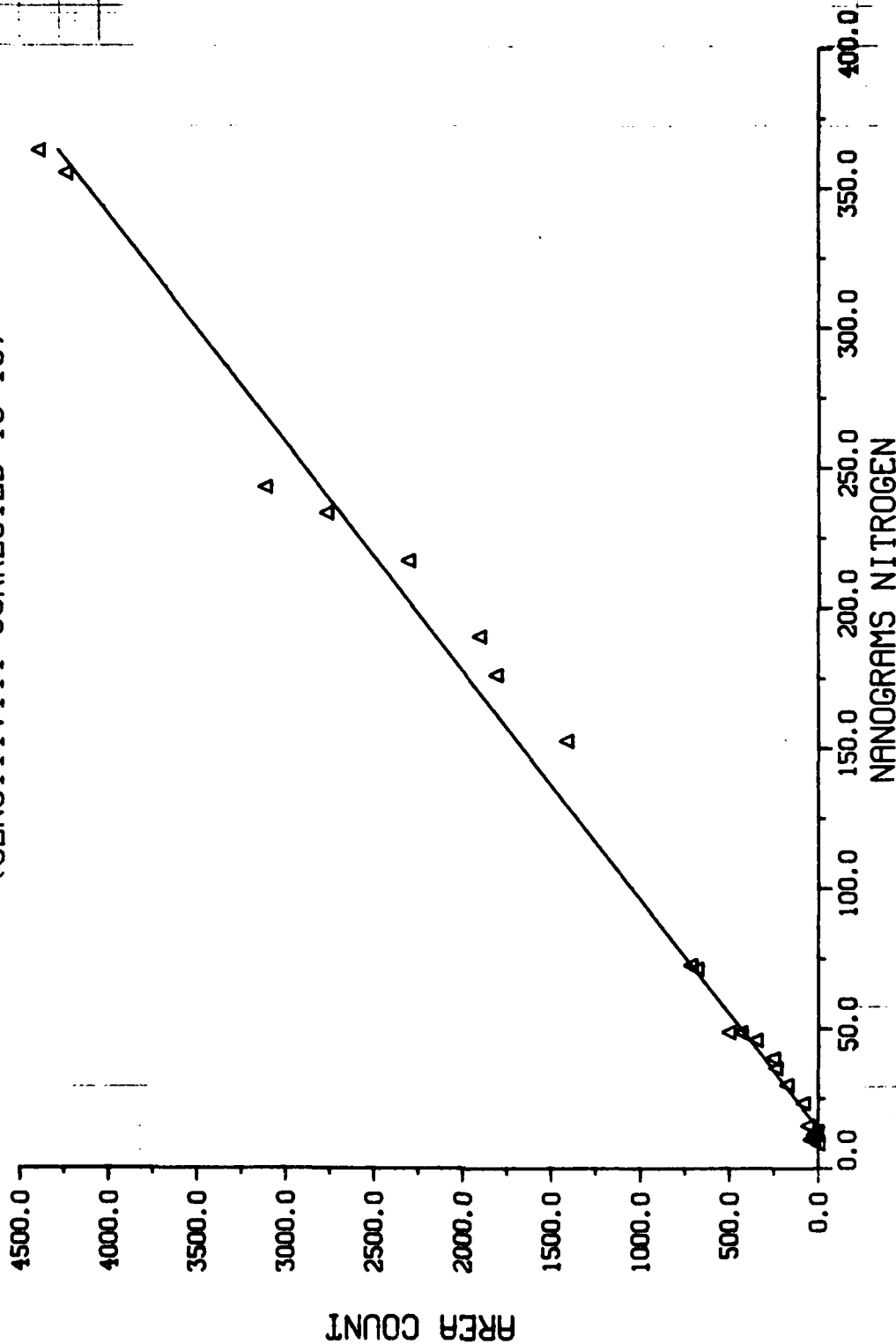


Figure 11. Mean Calibration Curve for ANTEK Nitrogen Analyzer (low ppm)

TABLE 4
KNOWN VS. MEASURED VALUES
FOR ADDITIONS TO SHALE FUEL

Code	Known Addition ppm	Measured Addition ppm
JP4-1	0 ppm	2 ppm
JP4-2	8.35 ppm	8.8 ppm
JP4-3	16.7 ppm	30.2 ppm
JP4-4	70.3 ppm	71.9 ppm
JP4-5	140.6 ppm	135.0 ppm
JP4-6	28.1 ppm	37.9 ppm

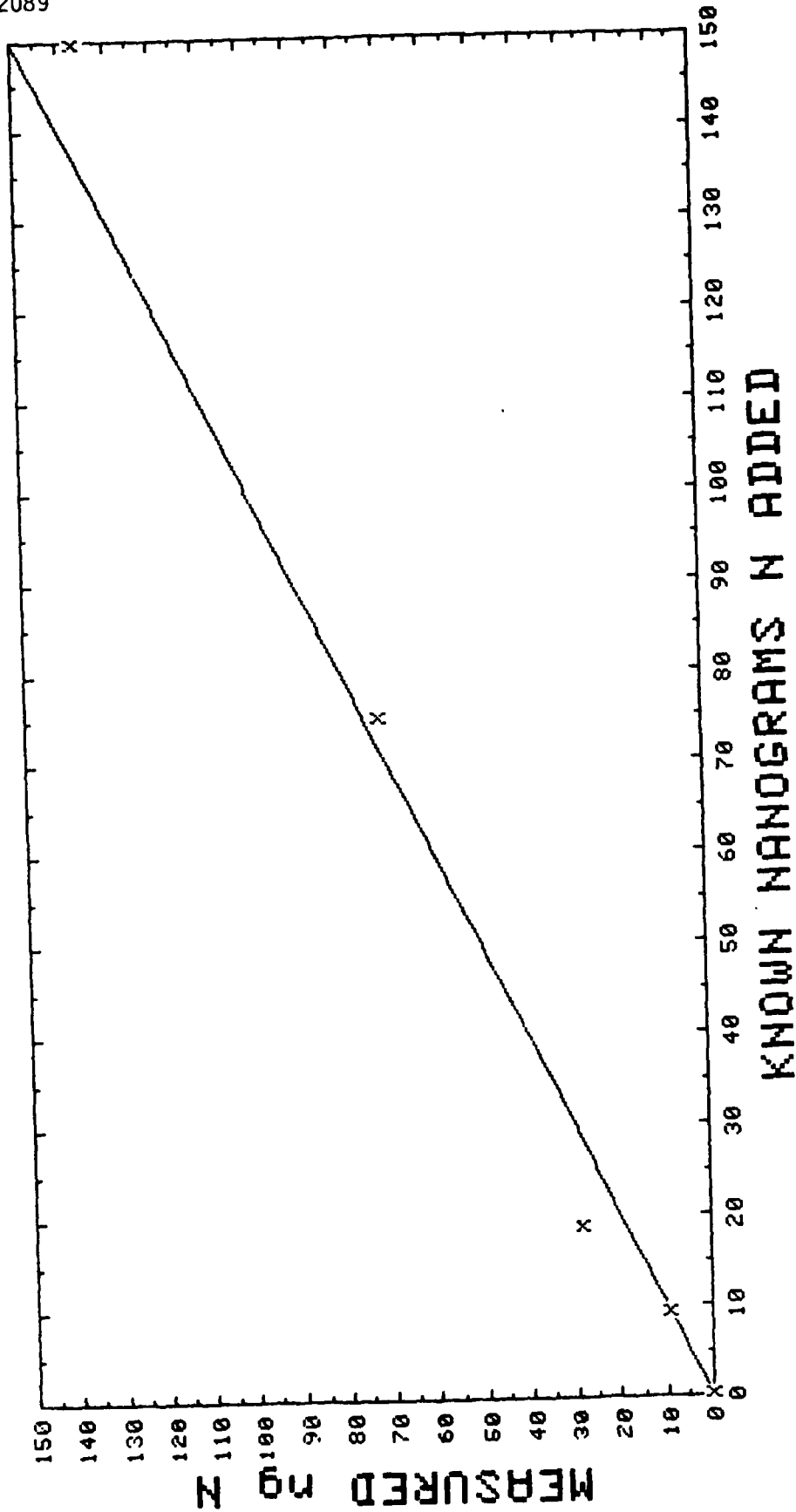


Figure 12. Known vs. Measured Nitrogen Addition for Shale Fuel Samples

SECTION III

DISCUSSION

1. MODEL MIXTURE STUDY

a. Linearity of Response with Concentration

The ANTEK Model 720 Chemiluminescent Nitrogen Detector shows excellent linearity of response according to concentration. Graphical analysis for five different concentrations of each nitrogen-bearing compound produces a linear fit with correlation coefficients of between 0.9996 and 0.9999.

b. Non-dependence on Compound Type

Figures 10 and 11 clearly indicate that detector response does not differ significantly with compound type. Thus, between 2 and 1500 ppm total nitrogen, the ANTEK analyzer is extremely effective in measuring total nitrogen content of a liquid, regardless of nitrogen type.

c. General Observations

The repeatability of detector response had to be determined at the very beginning of the project. Pyrrole in toluene standards were analyzed at two different times (three weeks apart) to demonstrate that there was very little drift in detector response. Figure 13 indicates a very slight change for the concentration range of 2 - 1500 ppm N. Figure 14, an expanded section of Figure 13, shows virtually no detector response change between 0 and 400 nanograms nitrogen during the three-week period.

One of the parameters that had to be closely monitored was the ozone flow rate. No repeatable results were obtained when the ozone rate was too low (approximately 60 cc/min instead of the preferred 120 cc/min). The ozone in the system tended to corrode lines and dissolve O-rings. Experimenters must ensure that needle valves for ozone control remain free of obstructions.

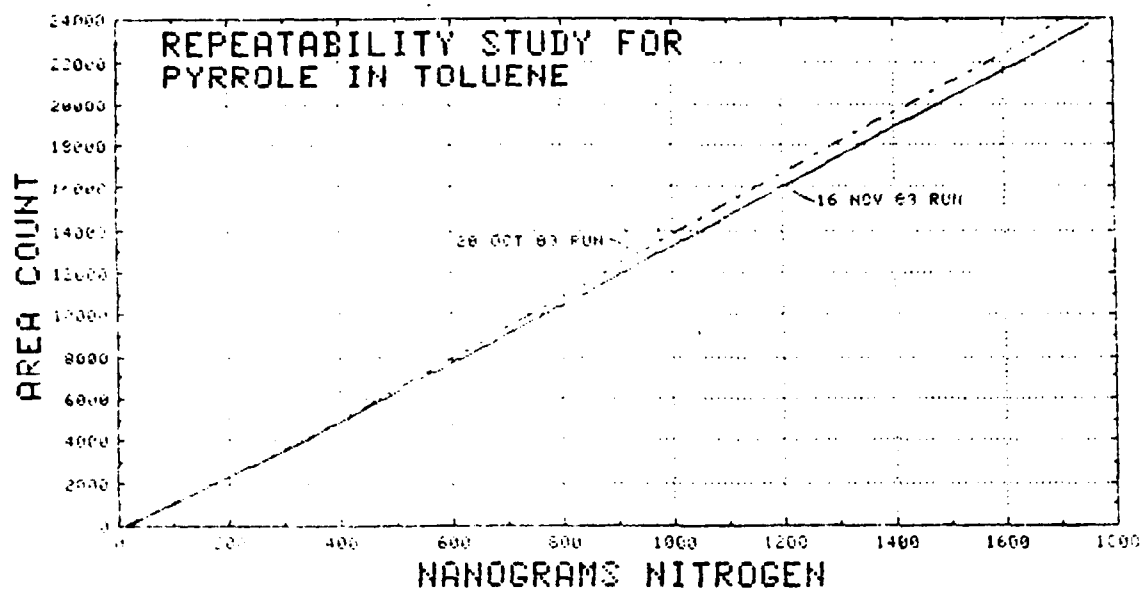


Figure 13. Repeatability Study for Pyrrole in Toluene

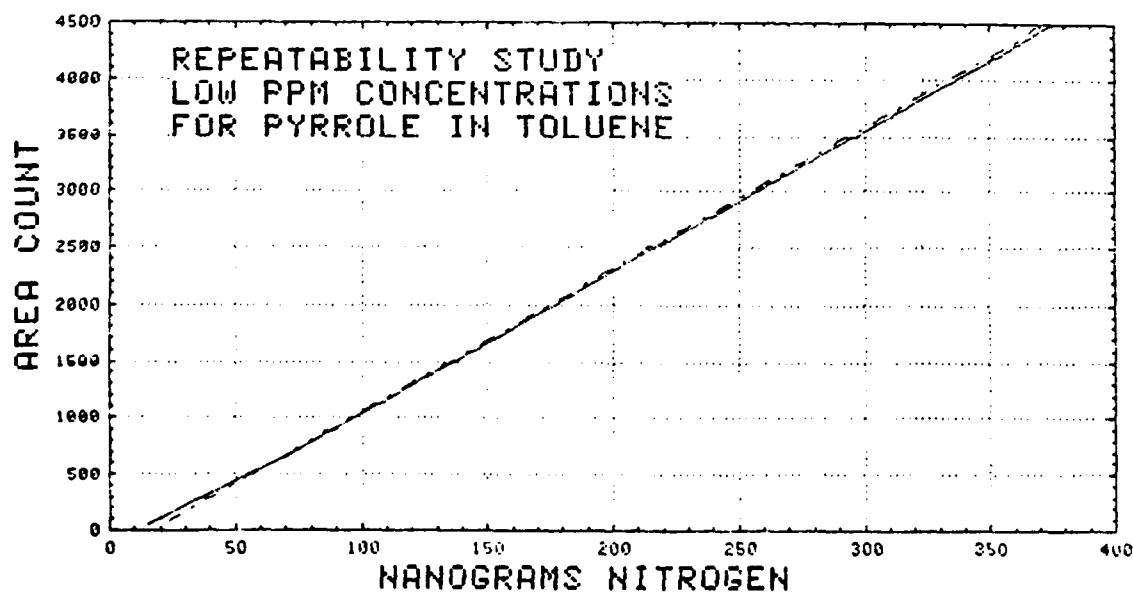


Figure 14. Repeatability Study: Low ppm Nitrogen

In order to analyze low parts-per-million solutions, i.e., less than 5 ppm nitrogen, a larger sample size is required. This larger sample size increases the amount of nitrogen injected, producing a greater detector response. Thus, it should be possible to analyze for total nitrogen in the parts-per-billion range merely by increasing the injection volume. Subsequent experiments, however, showed that this instrument cannot measure concentrations below 1 ppm nitrogen regardless of the sample size. Further investigations should be performed to document this preliminary work.

2. STANDARD ADDITIONS TO SHALE FUEL

Although the ANTEK analyzer accurately measured the nitrogen content of model mixtures, its ability to do so for samples with a complex hydrocarbon matrix had to be demonstrated. The fuel chosen for this experiment was a severely hydrotreated shale oil from the Caribou Refinery, Woods Cross, Utah. Since the fuel was so severely hydrotreated, it did not produce any area count when injected neatly into the ANTEK analyzer. This, of course, indicates little, if any, nitrogen in the fuel. Thus, the fuel was blended with five nitrogen-containing standard solutions to bring the concentration of N to a measurable level (Table 3). The results of the experiment show that the ANTEK chemiluminescent detection system can accurately measure nitrogen, even in a complex hydrocarbon matrix such as a shale derived turbine fuel.

3. COMPARISONS OF CHEMILUMINESCENCE TO OTHER METHODS OF NITROGEN ANALYSIS

Chemiluminescence seems to be the method of choice for many because of its short analysis time and its high accuracy. In order to see how accurately this instrument predicted the nitrogen level of the shale-derived JP-4 samples, another experiment was conducted. One pint from each sample (JP4-1 through JP4-6) was sent to four different commercial laboratories for nitrogen analysis with their best method. The Perkin-Elmer 240C was used by one laboratory but was found to be ineffective at the low concentrations used in this experiment (Table 5). The microkjeldahl method was accomplished by two separate laboratories and gave fair results. Note that the results were especially good from the analysis by Laboratory A, but not especially accurate by Laboratory C. The chemiluminescent method was the method used by Laboratory B; this instrument is a more recent model than the instrument described in this report. As can be seen, the results from this Monsanto instrument compare very favorably to those obtained on the Air Force unit.

TABLE 5
NITROGEN ANALYSES OF SHALE FUELS

Sample	Microkjeldahl, ^a			Antek, ^b			Perkin-Elmer 240, ^c			Antek ^d ppm	Known Additions
	(1)	(2)	(Avg)	(1)	(2)	(Avg)	(1)	(2)	(Avg)		
(JP4-1) 83-POSF-1572	32	31	32	1	1	1	0	400	-	2	0
(JP4-4) 83-POSF-1573	92	84	88	68	69	69	100	0	-	71.9	70.3
(JP4-3) 83-POSF-1574	28	25	27	27	27	27	100	0	-	30.2	16.7
(JP4-6) 83-POSF-1575*	47	41	44	40	39	40	100	100	100	37.9	28.1
(JP4-5) 83-POSF-1576	125	116	121	137	134	136	0	100	-	135.0	140.6
(JP4-2) 83-POSF-1577	57	60	59	20	19	20	200	0	-	8.8	8.35

^aResults from Laboratory A.

^bResults from Laboratory B.

^cResults from Laboratory C.

^dResults from WPAFB.

*Iso-octane (2,2,4-trimethylpentane) used as solvent.

SECTION IV

RECOMMENDATIONS

It is highly recommended that the Air Force use a chemiluminescent detector to measure the nitrogen level in aviation turbine fuels. If levels of nitrogen are below 1500 ppm, the chemiluminescent method is the best available in terms of accuracy, precision, and ease of operation. Greater concentrations of nitrogen can also be measured using this instrument by diluting a sample in solvent. One of the reasons for increased interest in this instrument has been the Air Force's Shale Fuel Validation Program. The purpose of this program has been to develop jet fuel resources in an operational environment. Since the shale crude is high in organically bound nitrogen and nitrogen is a suspected cause of thermal instability, it is certainly necessary to monitor this parameter during production as well as at the base level. Using the ANTEK nitrogen analyzer as a quality assurance instrument for this program is highly recommended.

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